(19) Europäisches P[illegible]amt
European Patent Office
Office uropéen des brevets

(11) Publication number: **0 250 631 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **86109013.2**

(22) Date of filing: **02.07.86**

(51) Int. Cl.⁴: **C03C 25/02**, C09D 3/80, C08F 299/06

(43) Date of publication of application: **07.01.88 Bulletin 88/01**

(84) Designated Contracting States: **BE DE FR GB IT NL SE**

(71) Applicant: **DeSOTO, INC.**
1700 South Mt. Prospect Road
Des Plaines Illinois 60018(US)

(72) Inventor: **Bishop, Timothy E.**
1720 Riverwood Drive
Algonquin, Ill. 60102(US)

(74) Representative: **Reitzner, Bruno, Dr. et al**
Patentanwälte Dipl.-Ing. R. Splanemann Dr. B. Reitzner Tal 13
D-8000 München 2(DE)

(54) Ultraviolet curable buffer coatings for optical fiber.

(57) An ultraviolet curing liquid coating composition is disclosed which, when cured with ultraviolet light in the presence of a photoinitiator, provides a buffer coating for optical glass fiber having adequate strength at room or expected elevated temperature and stability at such elevated temperature, a high index of refraction above 1.48, and a low tensile modulus which remains low to resist microbending difficulties down to around -60°C. This coating composition consists essentially of a linear polyacrylate-terminated polyurethane oligomer in admixture with a liquid linear aliphatic diacrylate in which the two acrylate groups are separated by a molecular weight of at least 400 to about 4000, said liquid linear diacrylate providing said coating composition with a viscosity suitable for coating application.

EP 0 250 631 A1

terminated polyurethan oligomer (which may be of various type, including that disclosed in the Ansel application, but which is preferably of the type disclosed hereinafter which is also a polyurea) in admixture with a relatively high molecular weight liquid linear aliphatic diacrylate in which the two acrylate groups are separated by a linear chain containing at least 6 carbon atoms, or where less than 6 carbon atoms are present in the chain, that chain has a molecular weight of from 400 to about 4000, preferably from 600 to 2500. Polyoxyalkylene glycol diacrylates are preferred, especially polyoxybutylene glycol diacrylates having a molecular weight of from 800 to 2000. The above polyacrylate-terminated oligomer is preferably based on a diisocyanate in which a linear aliphatic chain containing at least 6 carbon atoms separates the two isocyanate groups, and this diisocyanate is reacted with a polyether or polyester containing alkylene groups having from 1 to 6 carbon atoms and a molecular weight in the range of 500 to 4000, to form a polyurethane diisocyanate which is half end capped with a monohydric acrylate and reacted with a C_1 to C_4 oxyalkylene diamine having a molecular weight of from 100 to 600 to consume the isocyanate groups.

The compositions of this invention normally have an index of refraction above 1.48, and possess a tensile modulus far lower than was previously obtainable using the teachings of the said Ansel application. As a result, microbending difficulties are now avoidable down to around -60°C.

Referring more particularly to the linear polyacrylate-terminated polyurethane oligomer which is used herein, these may be the same as those taught in the prior Ansel application and have a molecular weight of about 2000 to about 8000 with one linking group selected from urethane, urea or amide groups for every 300 to 900 units of weight, but it is preferred to employ oligomers which are based on a diisocyanate in which a linear aliphatic chain containing at least 6 carbon atoms separates the two isocyanate groups. Any long chain aliphatic diisocyanate can be used, such as 1,12-dodecyl diisocyanate. The preferred diisocyanates are dimer fatty acid diisocyanates. Dimer fatty acids are dicarboxylic acids formed by dimerizing fatty acids which usually contain 18 carbon atoms, and this provides a 36 carbon atom dicarboxylic acid. When these two terminal carboxylic acid groups are converted to isocyanate groups, the r sult is a C_{36} diisocyanate.

The separation of the two isocyanate groups may include other groups in addition to the long carbon chain. Thus, dimer fatty acids may be reacted with ethylene oxide to provide hydroxy ester groups, or with several moles of ethylene oxide to add ether groups, and then the hydroxy-terminated product so-provided can be reacted with excess diisocyanate to provide isocyanate terminal groups. Also, the two carboxy groups in the starting dimer fatty acid can be converted to amine groups in known fashion, and the resulting diamine can be reacted with excess diisocyanate to provide a diisocyanate which still contains the 36 carbon atoms chain which has been found to provide the new properties desired herein.

The above long chain aliphatic diisocyanate is reacted with a polyether or polyester containing alkylene groups having from 1. to 6 carbon atoms (preferably 2 or 3 carbon atoms) and a molecular weight in the range of 500 to 4000. It is preferred to employ polyoxyalkylene glycols having a molecular weight in the range of 1000 to 3000, and in which the alkylene groups contain from 1-4 carbon atoms. These are illustrated by polyoxyethylene glycol having a molecular weight of 1500, 2000 or 2500, polyoxypropylene glycol of corresponding molecular weight, and polytetramethylene glycol of molecular weight 1000. Polyoxyethylated or polyoxypropylated diols, such as butane diol, hexane diol, polyoxyethylene glycol or polyoxypropylene glycol, are also useful.

Polyesters which may be used are illustrated by polycaprolactone glycols, such as the commercially available Tone 0240 from Union Carbide Corporation which is a polycaprolactone glycol having a molecular weight of about 2000.

The reaction between the previously described diisocyanate, which is used in an excess of preferably one mole of diisocyanate per hydroxy group, and the glycol forms a polyurethane diisocyanate.

The above polyurethane diisocyanate is then half end capped with a monohydric acrylate, such as a C_2 to C_4 hydroxyalkyl acrylate. Any monohydric acrylate may be used to end cap the isocyanate functional oligomers used herein, typically 2-hydroxyethyl acrylate. 2-hydroxypropyl acrylate and 2-hydroxybutyl acrylate are also useful. Trimethylol propane diacrylate or pentaerythritol triacrylate will further illustrate the class of useful monohydric alcohols.

The half end capped diisocyanate is reacted with a C_1 to C_4 oxyalkylene diamine having a molecular weight of from 100 to 600 to consume the remaining isocyanate functionality. The sequence of reactions is not important, for end capping can precede, follow or be simultaneous with the reaction with the diamine. As is well known, the diamine will form two urea groups, one from each of the two amine groups, to chain extend the half end capped diisocyanate (which is an unsaturated monoisocyanate). Typical diamines are amine-terminated polyethers, such as polyoxyethylene, or preferably polyoxypropylene, with the polyether chain providing the bulk of the needed molecular weight.

grams of dimethylaminoethyl acrylate are then added over a 20 minute period to reduce the viscosity with a monomer having a low glass transition temperature. 23.8 grams of 2-hydroxyethyl acrylate are then added over a 20 minute period and stirring is continued for an additional hour to end cap half of the diisocyanate-terminated polyurethane which is present. 24.5 grams of a polyoxyethylene diamine having a molecular weight of about 230 (Texaco product Jeffamine D230 may be used) are then added to the reactor and stirred at 60°C. until residual isocyanate functionality is no longer detectable. The added diamine provides one amine group per NCO group remaining in the reaction mixture, and the result is a diacrylate-functional polyurethane polyurea oligomer prepared from long-chain aliphatic materials.

67 parts of the above diacrylate polyurethane polyurea oligomer is mixed with 20 parts of a polyoxybutylene glycol diacrylate having a molecular weight of 1150 and catalyzed with 3 parts of Irgacure 651 and stabilized with 0.01 part of phenothiazine.

This composition was coated upon glass to form a film 3 mil thick which is cured by exposure to ultraviolet light using medium pressure mercury vapor lamps which supply ultraviolet light having a wavelength ranging from about 260 to about 380 nanometers. The ultraviolet dose is about 3.5 Joules/cm^2.

The cured films are stripped from the glass support and tested to provide the following data.

At 25°C. the tensile strength is 138 psi., the modulus is 303 psi. and the elongation is 58%. At -60°C., the tensile strength is 2889 psi., the tensile modulus is 52,800, and the elongation is 37%. These properties identify a clearly superior coating for the buffer coating of optical glass fiber when it is appreciated that the composition is stable at expected elevated service temperature and cures to provide a film having a refractive index of about 1.54.

In contrast, a typical commercial composition in accordance with the disclosure of said application Serial No. 170,148 coated and cured in the same way provides a film having a 25°C. strength of 500 psi, a tensile modulus of 500 psi., and an elongation of 170%. At -60°C., the tensile strength increased to 8700 psi., the modulus increased to 290,000 psi., and the elongation was only 5%. Thus, these cured coatings at -60°C. are much harder and more brittle than those obtained herein.

Using the diacrylate oligomer of this example in the typical commercial composition referred to above to provide a composition containing 63.11% of the diacrylate oligomer of this example, 24.27% phenoxyethyl acrylate, 9.70% N-vinyl pyrrolidone, 2.91% benzophenone, and 0.01% phenothiazine, the -60°C. tensile modulus was 177,300 psi. at an elongation of 25%. Replacing the monoethylenic monomers in this composition with the same weight proportion of the liquid diacrylate specified in this example, the -60°C. tensile modulus was lowered to 75,700 psi. and the elongation increased to 49%.

All of these coatings have about the same desirable refractive index of about 1.54.

The coatings of this invention are applied to freshly drawn optical glass fiber having a diameter of about 125 microns in a thickness of about 125 microns and are cured by passing the coated fiber through two tandemly arranged 10 inch 300 watts medium pressure vapor lamp at 1.5 meters per second.

Repeating the previous example using a lower molecular weight polyoxybutylene glycol diacrylate (calculated molecular weight of 800), the low temperature properties were very acceptable, albeit not quite as good as with the higher molecular weight product. Similarly, using a diacrylate in which an alkylene chain of 15 carbon atoms length is used as the liquid diacrylate, the low temperature properties were again acceptable, albeit not quite as good as when the two polyoxybutylene glycol diacrylates were employed.

Claims

1. An ultraviolet curing liquid coating composition which, when cured with ultraviolet light in the presence of a photoinitiator, provides a buffer coating for optical glass fiber having adequate strength at room or expected elevated temperature and stability at such elevated temperature, a high index of refraction above 1.48, and a low tensile modulus which remains low to resist microbending difficulties down to around -60°C., said coating composition consisting essentially of a linear polyacrylate-terminated polyurethane oligomer in admixture with a liquid linear aliphatic diacrylate in which the two acrylate groups are separated by at least a chain of 6 carbon atoms or by a molecular weight of at least 400 up to about 4000, said linear liquid diacrylate providing said coating composition with a viscosity suitable for coating application.

2. A coating composition as recited in claim 1 in which said two acrylate groups are separated by a molecular weight of from 600 to 2500.

3. A coating composition as recited in claim 2 in which said linear liquid diacrylate is a polyoxybutylene glycol diacrylate having a molecular weight of from 800 to 2000.

4. A coating composition as recited in claim 1 in which said polyacrylate-terminated polyurethane oligomer has a molecular weight of about 2000 to

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 10 9013

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 077 074 (DESOTO) * Claims; examples * ---	1,2,4-8	C 03 C 25/02 C 09 D 3/80 C 08 F 299/06
X	EP-A-0 125 710 (INTERNATIONAL STANDARD ELECTRIC) * Claims; examples * -----	1,10	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)
C 09 D C 08 F C 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03-02-1987	FOUQUIER J.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken al ne
Y : particularly relevant if combined with another document of the same category
A : technological background
O : n n-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for ther reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03 82